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(Commemoration Issue Dedicated to
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Structure and Activity of Vanadiumoxide(V)- Phosphorousoxide(V) Catalyst

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The promotive action of P_2O_5 in the binary system of V_2O_5 - P_2O_5 was investigated from structural point of view.

The addition of P_2O_5 into V_2O_5 in smaller amount than 5 mole% improved the catalytic activity for CO oxidation and made the catalyst easy to be reduced. On the other hand, the addition of more than 15 mole% of P_2O_5 caused the activity and reducibility of the catalyst to decrease.

The experimental results by x-ray diffraction, infrared spectroscopy and ESR absorption showed that the improvement of the activity was associated with the weakening of $V=O$ bond in V_2O_5 structure by the formation of the solid solution between V_2O_5 and small amounts of P_2O_5 , and that the decrease of the activity was associated with the reduction of the concentration of the active $V=O$ bond by the formation of some kinds of vanadyl phosphate.

INTRODUCTION

Vanadiumoxide(V) catalysts promoted with metal oxides such as molybdenumoxide, tungstenoxide, phosphorousoxide and potassiumoxide, are well known as good catalysts for oxidation of some hydrocarbons.¹⁾

As to the promotive action of these oxides, some investigators stressed the correlation between the catalytic activity and n-type semiconductivity.²⁾ This view can explain fairly many experimental results, but there are experimental facts that suggest another important factors must be considered to understand the action of these promoters. For example, sodium vanadium bronze whose electric conductivity is higher than vanadium oxide, is not so active for naphthalene oxidation.³⁾

In order to elucidate the action of these promoters, present authors have been studying the physico-chemical properties of various vanadiumoxide-metal oxide systems from structural point of view.⁴⁾ In this study, vanadiumoxide(V)-phosphorousoxide(V) system was investigated by means of x-ray diffraction, infrared spectroscopy and ESR absorption, and their catalytic activities for carbon monoxide oxidation and reducibilities by hydrogen were also measured and the promotive action of phosphorousoxide(V) was discussed.

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EXPERIMENTAL

1. Materials

Vanadiumoxide(V) (V_2O_5) was prepared by thermal decomposition of extra-pure grade ammoniummetavanadate in dry air at 450°C . This V_2O_5 was mixed with extrapure grade phosphorousoxide (P_2O_5) in a given ratio and melted in a crucible at 700°C for 30 mins. After cooling, the mixed samples were ground to powder in an agate mortar. The compositions of catalysts are tabulated in Table 1.

Table 1. The Colour and Concentration of V^{4+} ions of Samples.

Sample No.	$V_2O_5 : P_2O_5$ mole ratio	color	$V^{4+}/V(\%)^*$
1	100 : 0	light orange	0.7
2	99 : 1	dark orange	—
3	95 : 5	dark orange	1.5
4	85 : 15	brown	5.54
5	75 : 25	dark brown	5.64
6	67 : 33	dark brown	6.93
7	50 : 50	(yellow) ocher	14.9
8	33 : 67	yellow green	18.4
9	25 : 75	blue green	33.3
10	10 : 90	light blue green	47.6
11	0 : 100	white	—

* by chemical analysis

Carbon monoxide (CO) was obtained by decomposition of extrapure grade formic acid and the reactant gas for CO oxidation was prepared by mixing of CO and air in the ratio air/CO=4.

Hydrogen (H_2) from a commercial bomb was used for reduction of the catalysts after purification.

2. Apparatus and Procedure

X-ray diffraction experiments were carried out by a Nolelco x-ray diffractometer with Cu target at room temperature. Magnetic susceptibilities were measured by the Gouy method at magnetic field of 11,050 Oe at room temperature. ESR spectra of the powder samples were obtained by a x-band spectrometer manufactured by the Tokyo Denki Seiki Co., and infrared spectra of the samples dispersed in KBr disks were recorded on a Hitachi E. P. II model spectrometer.

The reduction process of catalyst by H_2 was followed by measuring the weight decrease of the sample. For this purpose, a torsion balance manufactured by the Shimadzu Co. was used under following conditions; amount of catalyst sample, 500 mg, feed rate of H_2 , 125 ml/min, temperature range, $420^\circ\text{--}490^\circ\text{C}$. (It was ascertained that the diffusion process in gaseous phase had no effect on the reduction under these conditions.)

The catalytic activity for CO oxidation was measured by the conventional flow method with 500 mg of catalysts at temperature range from 435 to 540°C and atmospheric pressure. The reacted gas was analyzed by a Orsat apparatus.

EXPERIMENTAL RESULTS

1. X-ray diffraction

X-ray diffraction diagrams of V_2O_5 - P_2O_5 samples of various compositions are shown in Fig. 1. The essential features of the diagrams of the samples which

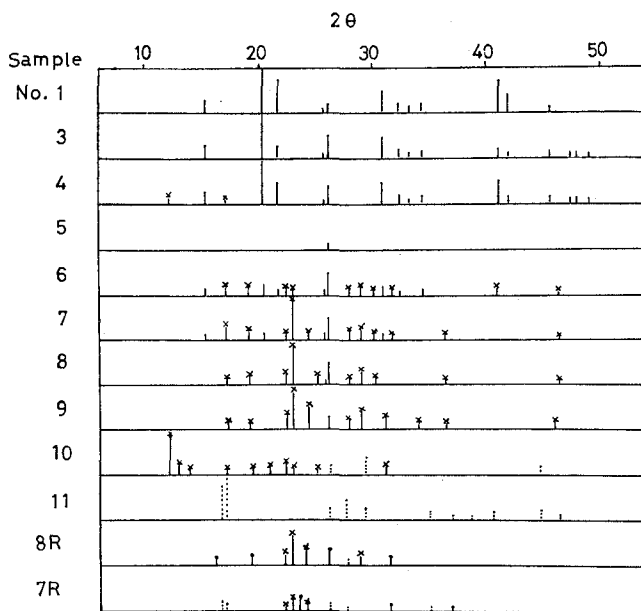


Fig. 1. X-ray diffraction diagrams of V_2O_5 - P_2O_5 .
No. of samples are shown in Table 1.
No. 8R: No. 8 was reduced at 480°C for 4 hrs.
No. 7R: No. 7 was reduced at 480°C for 10 hrs.

contain P_2O_5 less than 15 mole% are almost identical. Only observable change is that the diffraction line of $2\theta=20.25^\circ$ (corresponding to $d=4.38 \text{ \AA}$, the spacing along c axis of V_2O_5 unit cell) shifted to $2\theta=20.40^\circ$ (corresponding to $d=4.36 \text{ \AA}$). The sample of No. 5 (V_2O_5 3 : P_2O_5 1) did not show distinct diffraction lines, but only one broad weak peak. This fact means that this sample is almost in an amorphous state. The diffraction patterns of the samples which contain P_2O_5 more than 33.3 mole% are mainly composed of some diffraction lines marked with * which can be attributed to neither V_2O_5 nor P_2O_5 .

These diffraction lines are probably ascribed to that of some kind of vanadyl phosphate and some of these lines are observed even after reduction as shown in Fig. 1 (No. 7R and No. 8R).

2. Magnetic susceptibility

In Fig. 2 the variation of magnetic susceptibility (χ_g) with the composition

Vanadiumoxide(V)-Phosphorousoxide(V) Catalyst

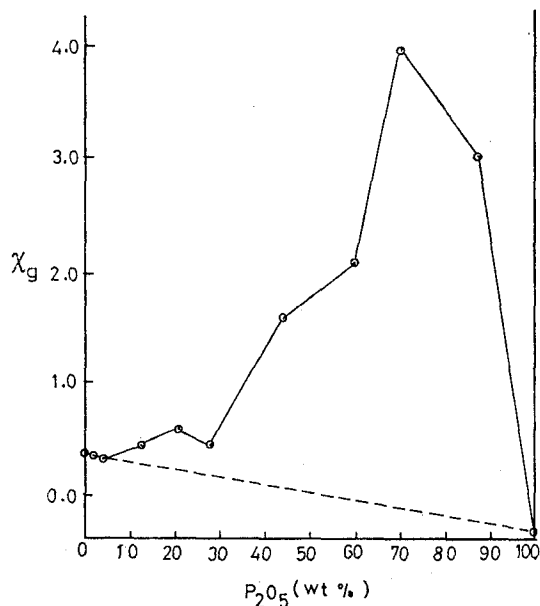


Fig. 2. Magnetic susceptibility of V₂O₅-P₂O₅.

of samples is shown. The dashed line in the figure shows the expected value of the mechanical mixture of V₂O₅ and P₂O₅. The observed values for the samples which contain more than 15 mole% of P₂O₅ deviate to larger value region of χ_g from this line. The deviation is especially remarkable in the case of the sample in which concentration of P₂O₅ is more than 50 mole%. This variation of χ_g corresponds with the change of the V⁴⁺-concentration shown in Table 1.

3. ESR absorption spectra

For all samples except pure P₂O₅, ESR absorption were observed as shown in Fig. 3 and the samples which contained from 5 to 25 mole% of P₂O₅ showed the spectra composed of hfs with a broad absorption as a back ground. A typi-

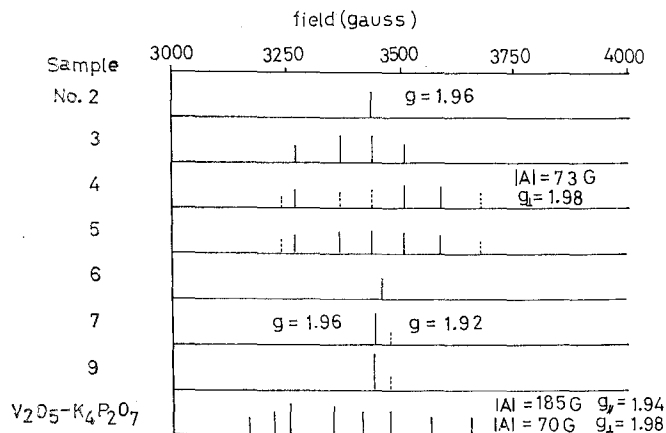


Fig. 3. ESR absorption diagram of V₂O₅-P₂O₅.

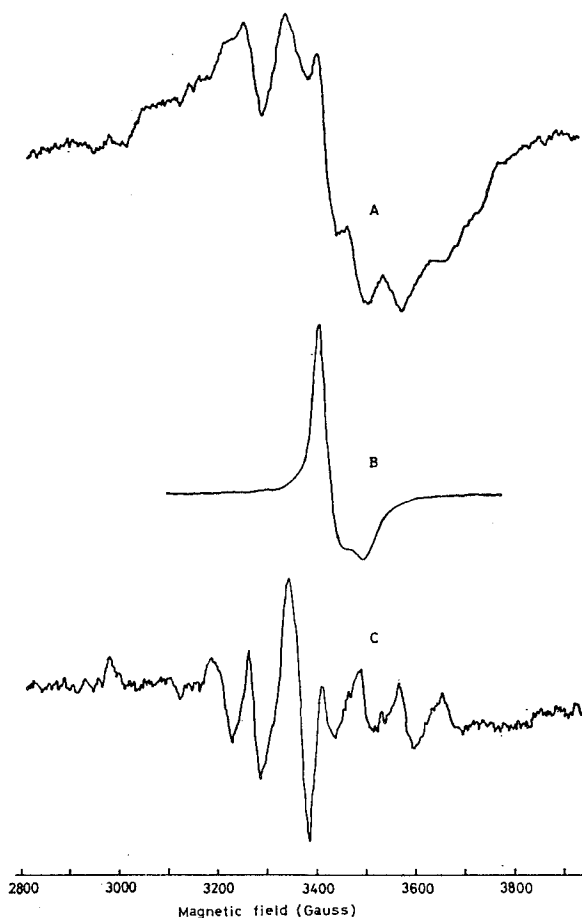


Fig. 4. ESR absorption spectra of V_2O_5 - P_2O_5 .
 A: No. 5 (cf. Table 1)
 B: No. 7 (cf. Table 1)
 C: V_2O_5 - $K_4P_2O_7$ (40:60 mole%)

cal spectrum shown in Fig. 4A is resemble to that of V_2O_5 - K_2SO_4 -diatomaceous earth catalyst after being used for SO_2 oxidation.⁵⁾

On the other hand, the ESR spectra of samples of No. 6~9, for which new x-ray diffraction lines were observed, consisted of two absorption peaks probably due to g anisotropy (Fig. 4B). In Fig. 4C the ESR spectrum of V_2O_5 - $K_4P_2O_7$ (40:60) is shown for comparison and this is composed of two set of well resolved hfs with coupling constants of 185G and 70G respectively.

4. Infrared absorption spectra

As previously reported, two infrared absorption bands have been observed for V_2O_5 in the range of 2000 to 650 cm^{-1} . The one, the center of which is at 1025 cm^{-1} , can be assignable to the stretching vibration mode of $V^{5+}=O^{2-}$ bond.⁶⁾ By adding P_2O_5 less than 15 mole%, this absorption band shifted to lower wave number region and reached to 1020 cm^{-1} . Absorption spectra of these samples,

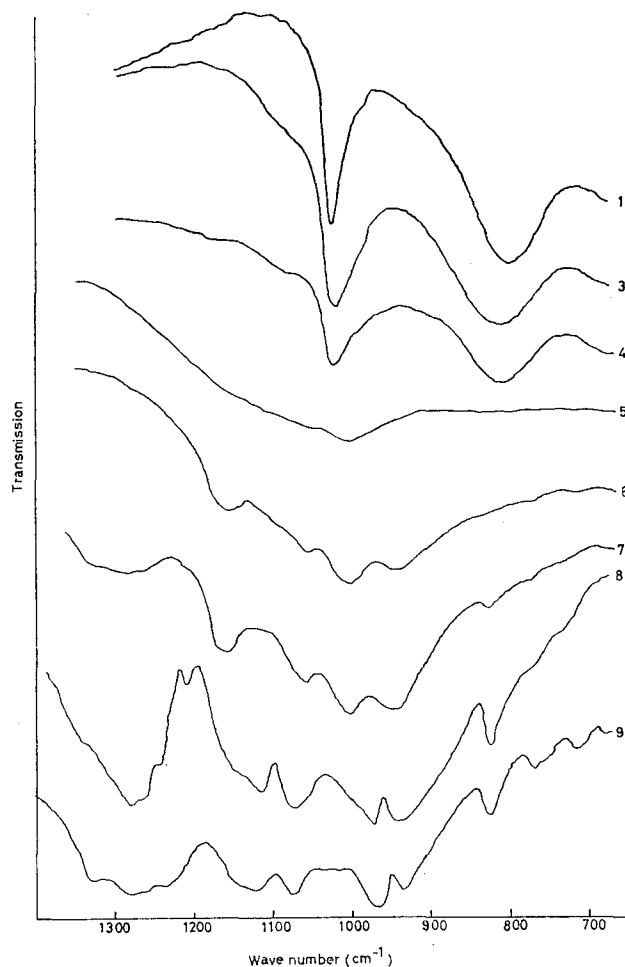
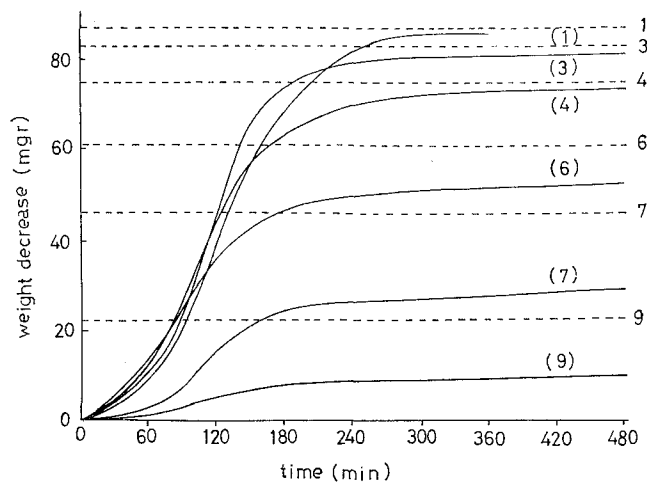


Fig. 5. Infrared spectra of V_2O_5 - P_2O_5 .
(No. of spectrum corresponds with No. of sample in Table 1.)

however, were identical as a whole to that of V_2O_5 as shown in Fig. 5. When samples contained more than 15 mole% of P_2O_5 , new bands were observed showing formation of some new compounds (Fig. 5). One of these bands, the center of which was at 1000 cm^{-1} , was very broad and may be due to perturbed VO^{2+} ion.⁷⁾ The sample No. 5 showed only this broad absorption band at 1000 cm^{-1} . In the spectra of the samples which contained more than 50 mole% of P_2O_5 , an absorption band at 1260 cm^{-1} due to $P=O$ bond⁸⁾ was observed.

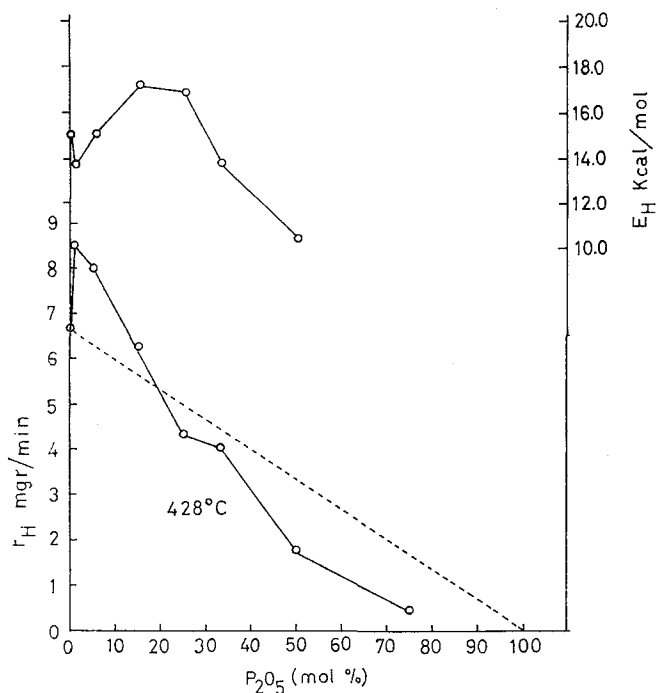
5. Reduction by H_2

It is known that V_2O_5 is reduced to V_2O_3 by H_2 and its rate is expressed by "parabolic law".⁹⁾ In Fig. 6 the weight decrease with time is shown for some V_2O_5 - P_2O_5 samples in the stream of H_2 at 428°C . In this figure, dashed lines stand for the expected values if each sample is reduced to V_2O_3 - P_2O_5 mixture. Apparently, the samples containing P_2O_5 less than 15 mole% had the same character as pure V_2O_5 to the reduction by H_2 . In the case of sample in which

Fig. 6. Reduction of V_2O_5 - P_2O_5 by H_2 at $428^\circ C$.

concentration of P_2O_5 was large, the rate of reduction became slower and the amount of weight decrease at equilibrium was smaller than the expected value mentioned above. In fact, the x-ray diffraction pattern of the sample No. 7 (P_2O_5 50 mole%) showed that the new compound in the sample remained even after treatment with H_2 for 16 hrs at $480^\circ C$.

For the comparison of reducibility of each sample, the maximum slope (r_H) of each line in the Fig. 6 was taken as a measure of the reduction rate. The

Fig. 7. Reduction of V_2O_5 - P_2O_5 by H_2 .

variation of r_H at 428°C and the apparent activation energy E_H are shown in Fig. 7.

The dashed line in Fig. 7 shows the expected decrease of r_H by dilution effect with adding of P_2O_5 and larger value of r_H than that of this line reveals the increase of reducibility. The samples of No. 2, 3 and 4 are more easily reduced than V_2O_5 .

6. Catalytic activity for CO-oxidation

As a linear relation between conversion (%) of CO to CO_2 and contact time was observed up to 30% conversion, the activity was indicated by the conversion % of CO (r_{CO}) at contact time 1.5 sec. The activity at 485°C and the apparent activation energy (E_{CO}) for each catalyst are shown in Fig. 8. The dashed line in Fig. 8 shows the expected variation of activities (r_{CO}) with decrease of V_2O_5 contents by adding of inactive P_2O_5 . The addition of small amount of P_2O_5 promotes the catalytic activity of V_2O_5 .

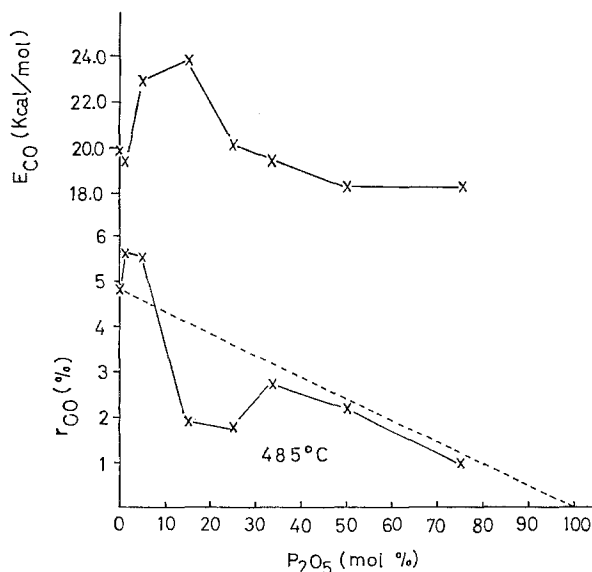


Fig. 8. CO oxidation by V_2O_5 - P_2O_5 .

DISCUSSION

1. The physico-chemical properties of V_2O_5 - P_2O_5 system

To discuss the physico-chemical properties of this system, it seems to be convenient to divide the system into three regions with regard to P_2O_5 content.

The first region is the one in which the concentration of P_2O_5 is less than 15 mole% and x-ray diffraction patterns as well as infrared absorption spectra exhibit the existence of the solid solution of substituted type as a main crystal phase. It can not be expected that the formation of solid solution in this system accompanies the increase of V(IV) ions by so called "principle of controlled valency", because the valence state of phosphor is five. In fact, the magnetic susceptibility (χ_g) which corresponds to amounts of V(IV) ions changed as if

the samples were simple mechanical mixture of V_2O_5 and P_2O_5 in this region. A slight increase of κ_g at the concentration of No. 4 (15 mole% P_2O_5) may be due to the formation of some amorphous compounds which contain four valent vanadium as VO^{2+} ions. This assumption is also supported by ESR measurements. The ESR spectra for the samples of No. 3 (5 mole% P_2O_5)~No. 5 (25 mole% P_2O_5) composed of the characteristic hfs of VO^{2+} as shown in Fig. 3 and this fact can be interpreted as VO^{2+} ions existed in an amorphous phase with weak interaction each other.¹⁰⁾

In the case of V_2O_5 - MoO_3 system, it was found that the infrared absorption band due to $V=O$ bond shifted to the lower wave number region with increase of MoO_3 content within the limit of formation of solid solution and the shift was associated with the formation of $V(IV)$ ions. In the present case, also, the same kind of shift was observed, but as mentioned above, there is no special increase of $V(IV)$ ions with doping P_2O_5 . Therefore, the reason of the shift might be caused by distortion of crystal lattice mainly due to the difference of ionic radii. (cf. Ionic radii of $V(V)$ and $P(V)$ are 0.59 and 0.34 Å, respectively.¹¹⁾)

The second region is that in which P_2O_5 concentration is in the range of 15 to 30 mole%, and as shown in Fig. 1, the samples were amorphous compounds. The hfs in the ESR spectrum for the sample No. 5 is clearer than any other samples, and characteristic for vanadyl compounds.¹⁰⁾ On the other hand, V_2O_5 - $K_4P_2O_7$ (60 mole%) showed an ESR spectrum with hfs resolved as highly as V_2O_5 - $K_2S_2O_7$ samples as shown in Fig. 4C. So, the obtained compound may be alike to vanadyl phosphate and/or vanadyl pyrophosphate. The existence of infrared spectrum due to VO^{2+} for this sample supports the above explanation.

The samples which contain more than 30 mole% of P_2O_5 are in the third region. The x-ray diffraction measurements showed that there were two crystal phases, that is, the solid solution mentioned above and a new crystal phase which gave completely different diffraction pattern from that of V_2O_5 or P_2O_5 . The latter became to a main phase with increase of P_2O_5 concentration. Simultaneously, κ_g became remarkably large reaching to about 10 times that of V_2O_5 (Fig. 2). This means the new crystal compound comprises large amount of $V(IV)$ ions. Now, ESR spectra for the samples in this region were also quite different from that for the samples in foregoing two regions as shown in Fig. 3. The change in the spectra could be explained as the result of exchange narrowing induced by high concentration of $V(IV)$ ions. The formation of large amount of $V(IV)$ ions may result from that V_2O_5 is inserted into P_2O_5 matrix and forms some compounds which comprise of (VO^{2+}) or $(VO_4)_n$ tetrahedra linked together by sharing apexes.

2. The correlation between catalytic activity and structure

The variation of the catalytic activity with the composition in V_2O_5 - P_2O_5 system was already investigated by Margolis *et al.* for benzene oxidation reaction.¹²⁾ The present results approximately coincided with their experiments; the addition of P_2O_5 to V_2O_5 in small amount (less than 5 mole%) improved the catalytic activity for CO oxidation and reducibility. Margolis *et al.* related this

improvement of activity to the change of work functions of catalysts. The present investigation shows that the structural factors should be taken into account to elucidate the promotive action of P_2O_5 in V_2O_5 - P_2O_5 catalysts in analogy with V_2O_5 - MoO_3 binary catalysts.

In the previous works,⁴⁾ the authors pointed out that the $V=O$ bond on the surface of V_2O_5 plays an important role in the oxidation reaction and the promotive action of MoO_3 could be attributed to following two reasons. Thus, by adding MoO_3 to V_2O_5 less than 25 mole% (in the region of solid solution formation) 1) the $V=O$ bonds were weakened and 2) the crystal structure of V_2O_5 was stabilized.

In the present case of V_2O_5 - P_2O_5 , the analogous interpretation for the promotive action of P_2O_5 can be made by comparison with the catalytic activities and x-ray diffraction patterns as well as infrared spectra of samples. In the case of the catalysts in the first region, a solid solution was formed and the infrared absorption band due to $V=O$ bonds in V_2O_5 shifted to the lower wave number region and higher activities for CO oxidation than that of V_2O_5 were observed. However, the catalyst containing 15 mole% P_2O_5 (No. 4) showed lower activity than that of V_2O_5 , while x-ray diffraction pattern showed the main crystal phase was the same as V_2O_5 . The catalysts containing P_2O_5 by 5 to 25 mole% showed ESR spectra with hfs which are apparently associated with the formation of amorphous phase revealed by x-ray diffraction at the composition of P_2O_5 25 mole%. Thus the low activity of this catalyst No. 4 (P_2O_5 15 mole%) can be interpreted by the formation of a less active amorphous compound (alike to vanadyl phosphate) on the surface of the catalyst.

A close inspection of x-ray diffraction patterns revealed that in the catalyst in the third region, small portion of V_2O_5 -structure phase might be contributed to the restoration of the catalytic activity.

From the discussion mentioned above it may be presumed that the active sites of the investigated catalysts are $V=O$ bonds in V_2O_5 structure and $V=O$ bonds in vanadyl or vanadatophosphate (free VO^{2+} or $(VO_4)_n$) are less active for the catalytic oxidation. The presumption is consistent with the fact that the variation of activation energy with composition was small in this third region and the decrease of activity with increase of P_2O_5 content should be resulted from the decrease of frequency factor of rate constant. Thus the addition of P_2O_5 to V_2O_5 more than 30 mole% caused the decrease of active sites.

In conclusion, P_2O_5 should be added as promoter within the limit of the retention of the characteristic crystal structure of V_2O_5 .

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